

POLY(IMIDAZOPYRROLONES): A NEW ROUTE TO LADDER POLYMERS

by

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Introduction

Previous syntheses of aromatic-heterocyclic polymers have resulted in partial ladder ("step-ladder") macromolecular structures; i.e., condensed rings in the main chain which are separated by single links. Two of the most promising step-ladder polymers presently being developed and characterized are the polybenzimidazoles¹ (PBI) and the polyimides² (PI). In most cases these polymers have very short ladder segments, with no more than three fused rings between the single links. Theoretically, a greater degree of thermal stability for such polymers could be expected if the concentration of the single links are reduced by increasing the ring structures of the main chains³, ultimately leading to a complete ladder structure.

The ladder segments of the above polymers, and hence their thermal stabilities, result from the tetrafunctional monomers used in the polymerization: dianhydrides (tetraacids) in the case of the polyimides and ortho-tetraamines in the polybenzimidazole instance. Polymers which could be prepared by controlled polymerization of two or more polyfunctional monomers (e.g., dianhydrides or tetraacids and tetraamines) should have superior, thermal, oxidative and radiolytic stability. The classical dye chemistry literature provides the background for synthesis of some related model compounds. An especially attractive example is the reaction of o-phenylene diamine with aromatic anhydrides, such as

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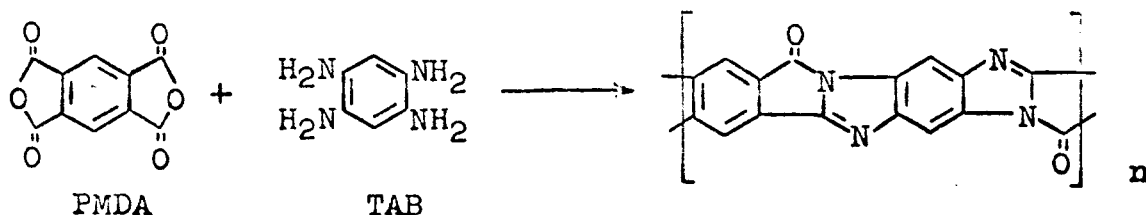
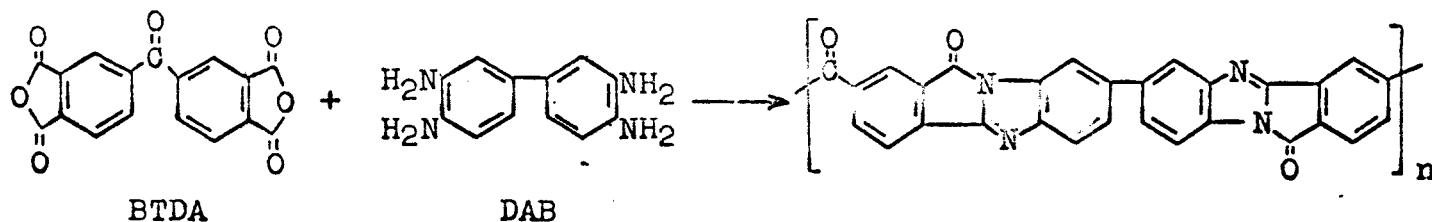
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1,8-naphthalic anhydride⁴ and phthalic anhydride⁵, which lead to the appropriate aroylene benzimidazoles.

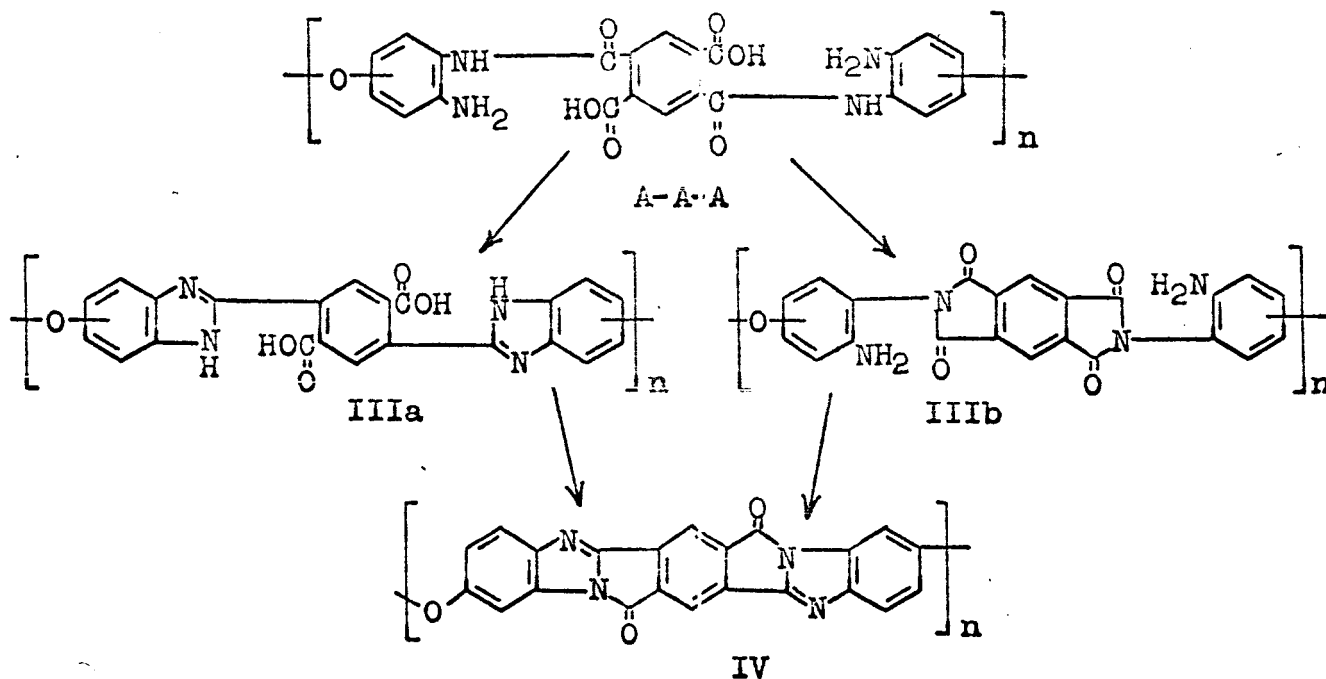
The extension of this reaction to aromatic dianhydrides and aromatic tetraamines has led to a new class of polymers, the poly(imidazopyrrolones), which can be prepared as ladder structures. The use of dianhydrides and/or tetraamines [e.g., 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 3,3'-diaminobenzidine (DAB)], has resulted in step-ladder polymers. Potentially complete ladder polymers have been realized by employing a dianhydride and a tetraamine [pyromellitic dianhydride (PMDA) and 1,2,4,5-tetraaminobenzene (TAB)] which have basic two-strand capabilities.



The versatility of this reaction scheme becomes apparent when the copolymer combinations which could result from combining various anhydrides and/or tetraamines are considered; numerous polymer systems with variable lengths of the fused ring structure and thus a range of polymer properties, have been prepared.

The general technique of polymerization involves the controlled reaction of the dianhydride with the tetraamine in a highly polar solvent,

such as dimethylformamide (DMF) and dimethylacetamide (DMAC). The room temperature reaction results in a slight temperature rise followed by a rapid increase in the viscosity. Adjustment of the viscosity of the solution to the desired level can be made by the addition of small incremental amounts of dianhydride. The initial polymer product, illustrated below for the reaction between PMDA and 3,3',4,4'-tetraaminodiphenyl ether (TADPO), is a poly(amide-acid-amine) (A-A-A). This polymer undergoes two consecutive dehydration steps when heated to give the final polymer IV, poly(oxy-7H, 15H-2,10-bis-benzimidazo[1,2-a: 1', 2'-a'] benzo [1,2-c: 4,5-c'] dipyrrol-7, 15-dione⁶. [Note: The designation of the positions is arbitrary since the exact mechanism has not been established.] For simplicity, we have referred to this class of polymers as "Pyrrones."



Experimental

Monomers and Solvents

Pyromellitic dianhydride (PMDA) [Hexagon Laboratories, Inc. and Princeton Chemical Research] and 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) [Gulf Chemical Corporation] were sublimed at 225-240°/0.5 mm. 3,3'-Diaminobenzidine (DAB) [American Aniline Products, Inc.] was purified by recrystallization from water. 1,2,4,5-Tetraaminobenzene tetrahydrochloride [Burdick and Jackson Laboratories, Inc.] was purified by dissolving in the minimum amount of water, treated with charcoal and reprecipitated with concentrated hydrochloric acid. 3,3',4,4'-Tetraaminodiphenyl ether (TADPO) was prepared by a modification⁷ of an earlier procedure⁸, using a precursor 4,4'-diamino-3,3'-dinitrodiphenyl ether, [Burdick and Jackson Laboratories, Inc.].

Solvents were purified by distillation from phosphorus pentoxide and, in certain cases, an additional distillation from pyromellitic dianhydride was performed.

Solution Polycondensation

Poly(Oxy-7H, 15H-2, 10-bis-benzimidazo[1,2-a: 1',2'-a'] benzo[1,2-c: 4,5-c'] dipyrrol-7, 15-dione) (IV)

The general procedure for polymerizing dianhydrides with tetraamines as the free base can be illustrated by the preparation of polymer IV. A solution of 4.20 g. (0.0192 mole) of PMDA in 40 ml. of DMF was added at once to a stirred solution of 4.60 g. (0.020 mole) of 3,3',4,4'-tetraaminodiphenyl ether in 35 ml. of DMF in a Waring Blendor. The solution thickened slightly and became warm (35-40°) within 15-20 seconds.

The stirring was continued for 5-10 minutes after which a portion of a solution of 0.30 g. (0.0014 mole) of PMDA in 5 ml. of DMF was added dropwise to the stirred polymer solution until the desired viscosity was obtained. The resulting thick polymer "dope" was centrifuged to remove bubbles and suspended matter. This polymer solution has been used for casting films, laminates, coatings, etc.

After the polymer was precipitated with acetone, it was collected by filtration, washed well with acetone, and dried under vacuum at room temperature. Calculated for $(C_{22}H_{16}N_4O_7)_n$ [poly(amide-acid-amine)]: C, 58.93; H, 3.60; N, 12.50; O, 24.98. Found: C, 56.03; H, 4.34; N, 12.54; O, 25.15. After heating this polymer at 425° for one hour, the analysis was as follows. Calculated for $(C_{22}H_8N_4O_3)_n$ [poly(imidazopyrrolone) (IV)]: C, 70.21; H, 2.14; N, 14.89; O, 12.76. Found: C, 63.29; H, 2.88; N, 14.77; O, 16.64.

Poly(imidazopyrrolone) from Pyromellitic Dianhydride and 1,2,4,5-Tetraaminobenzene (II)

Since 1,2,4,5-tetraaminobenzene is extremely susceptible to air oxidation, polymers from this tetraamine were prepared using the tetrahydrochloride salt. A solution of 4.36 g. (0.020 mole) of PMDA in 40 ml. of DMF was added slowly, in a dropwise fashion, to a stirred slurry of 5.68 g. (0.020 mole) of the hydrochloride salt in 35 ml. of DMF and 6.32 g. (0.080 mole) of pyridine. The polymerization mixture was blanketed at all times with nitrogen. The polymer was precipitated with aqueous ethanol and washed with acetone to remove pyridine hydrochloride, after which it could be redissolved in DMF.

Results and Discussion

The solubility of the A-A-A polymers made it possible to use classical solution techniques for characterization. In addition, this tractability of the Pyrrole prepolymers afforded a means to utilize the polymers for thin films, coatings and resins for composite structures. Films were obtained by casting the A-A-A solutions onto glass plates and the solvent was removed by heating in an oven under air or nitrogen at 125° for one hour. The amber films could be easily stripped from the glass plates. Further cyclization and condensation occurred with additional heating. After one hour at 225° the films were generally blood-red in color. After three hours at 325° the films were black by reflected light but very deep red by transmitted light. The films were clear, tough and flexible throughout the various stages of conversion.

Some preliminary properties of both the A-A-A and the converted Pyrrole polymers are shown in Table I.

Table I

Representative Properties of Poly(imidazopyrrolones)

<u>Solution Properties</u>	<u>A-A-A Stage</u>	<u>Pyrrole Stage</u>
Intrinsic Viscosity (25°, DMF)	0.6-1.5 dl/g	Insoluble
M _n (Osmotic Pressure)	7,000-20,000	"
Solvents	DMF, DMAC, NMP, DMSO, etc.	"
<u>Film Properties</u>		
Tensile Strength	10-15 kpsi	15-22 kpsi
Elongation	25-35%	3-7%
Young's Modulus	200-400 kpsi	600-1,000 kpsi
Specific Resistivity	6 x 10 ⁹ ohm-cm	3-5 x 10 ¹² ohm-cm
Field Strength	2 x 10 ⁵ v/cm	6 x 10 ⁵ v/cm

The data in Table II demonstrate the unusually high resistance of the Pyrrones to ionizing radiation. No significant effect on tensile properties was apparent even after 10,000 megarads.

Table II
Radiation Effects on PMDA-TADPO Pyrrone Films

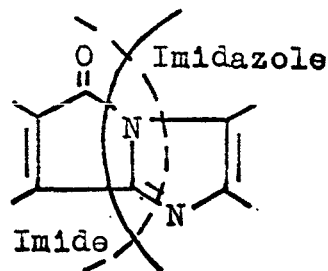
Dose* (Megarads)	Strength (kpsi)		Tangent Modulus (kpsi)	Elongation (%)
	Yield	Tensile		
Control	9.2	17.9	730	9
1,000	12.2	16.8	830	3
5,000	14.3	20.2	820	3
10,000	15.6	17.3	850	3

*1 Mev. electrons, 1,000 Mr/hr. Specimens degassed 72 hrs. at $50^{\circ}\text{C}/10^{-7}$ torr and sealed at 10^{-7} torr.

The infrared spectra of the polymers (Figure 1a and 1b) indicate that the mechanism leading to the final structure IV occurs through the formation of both the structures IIIa and IIIb concurrently. In figure 1a, the disappearance of secondary amide bands ($1650, 1540, 1280\text{ cm}^{-1}$), carboxyl bands ($1720, 1605, 1225\text{ cm}^{-1}$) and amino nitrogen-hydrogen bands (not shown) occurs progressively with heating and is accompanied by the development of imide ($1765, 720\text{ cm}^{-1}$) and imidazole (1620 cm^{-1}) bands.

Thermal Stability

The Pyrrones exhibit exceptional thermal stability as expected from consideration of the imidazopyrrolone moiety which is a coalescence of the most stable features of the polyimides and polybenzimidazoles.



The polymers do not burn in the usual sense or melt when exposed to flame. This stability is apparent in Figure 2 which shows the results of the thermogravimetric analysis of a PMDA-TADPO film (1 mil). The curve for a film of poly [N,N'-(p,p'-oxydiphenylene) pyromellitimide] (PI) obtained under essentially identical conditions is given for comparison. The gradual loss in weight of the Pyrrone up to 500°C. is probably due to expulsion of solvent (which forms a tenacious complex with the A-A-A unconverted polymer) and loss of water of condensation.

The unusual thermal stability of the Pyrrone polymer system is also evident in the elemental analyses. Carbon values were always abnormally low (3-7%) for the converted Pyrrones, perhaps because the combustion conditions employed in the analyses were inadequate to completely degrade the polymer and its subsequent graphitic structure. Corresponding analyses for pyrolytic graphite were found to yield carbon values 5% lower than theoretical. However, nitrogen analyses determined by the Kjeldahl method were close to theoretical and this was considered to be due to the fact that the method was independent of thermal behavior.

The exact molecular structure at each stage of conversion, and the kinetics and sequences of the reactions of tetraamines with dianhydrides are yet to be fully defined. In addition to these basic problems, further exploration of the useful properties of this new class of aromatic-heterocyclic polymers is presently being undertaken.

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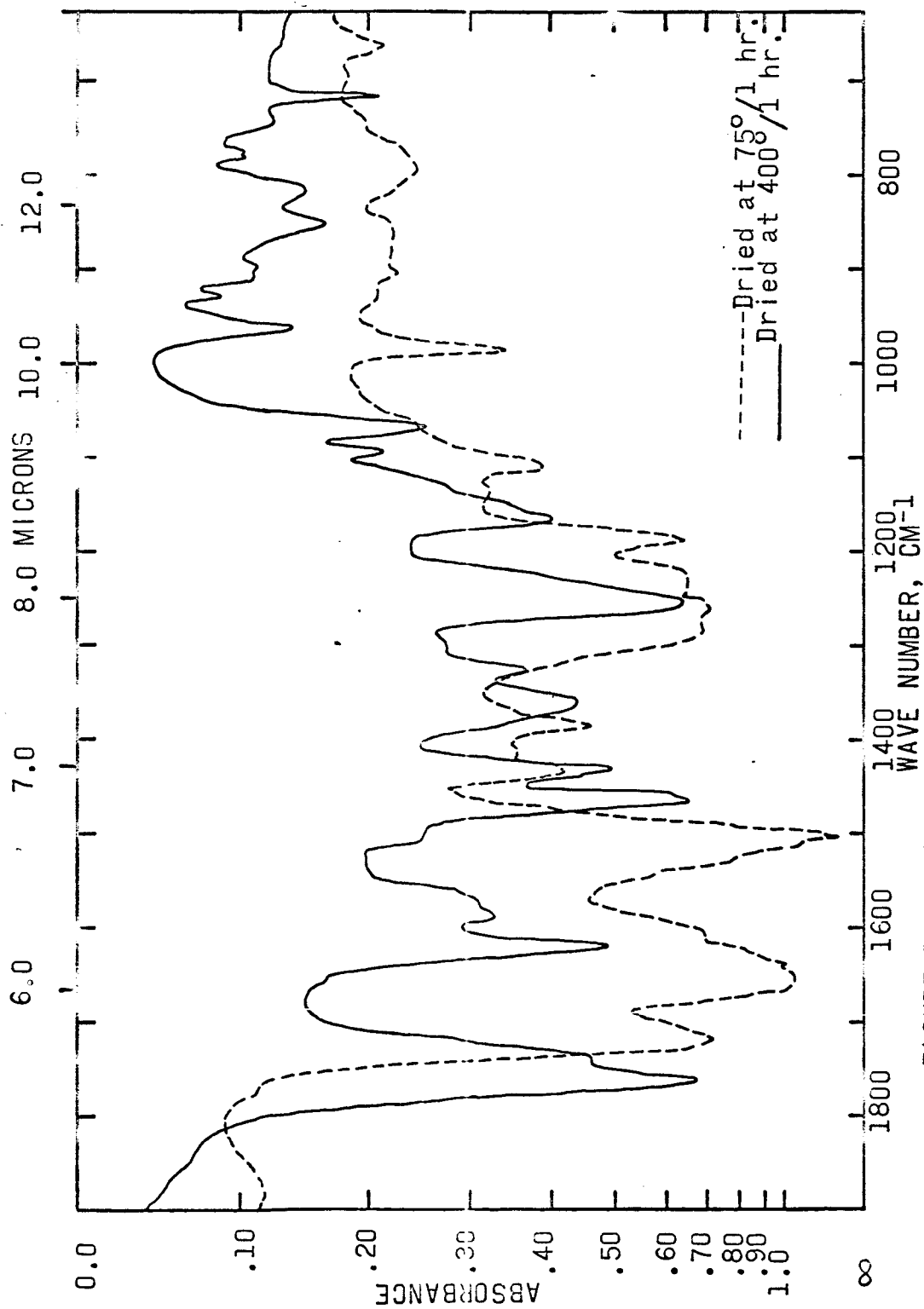


FIGURE 1a. - INFRARED SPECTRA OF PMDA-TADPO POLYMER FILMS, 0.15 MIL THICK

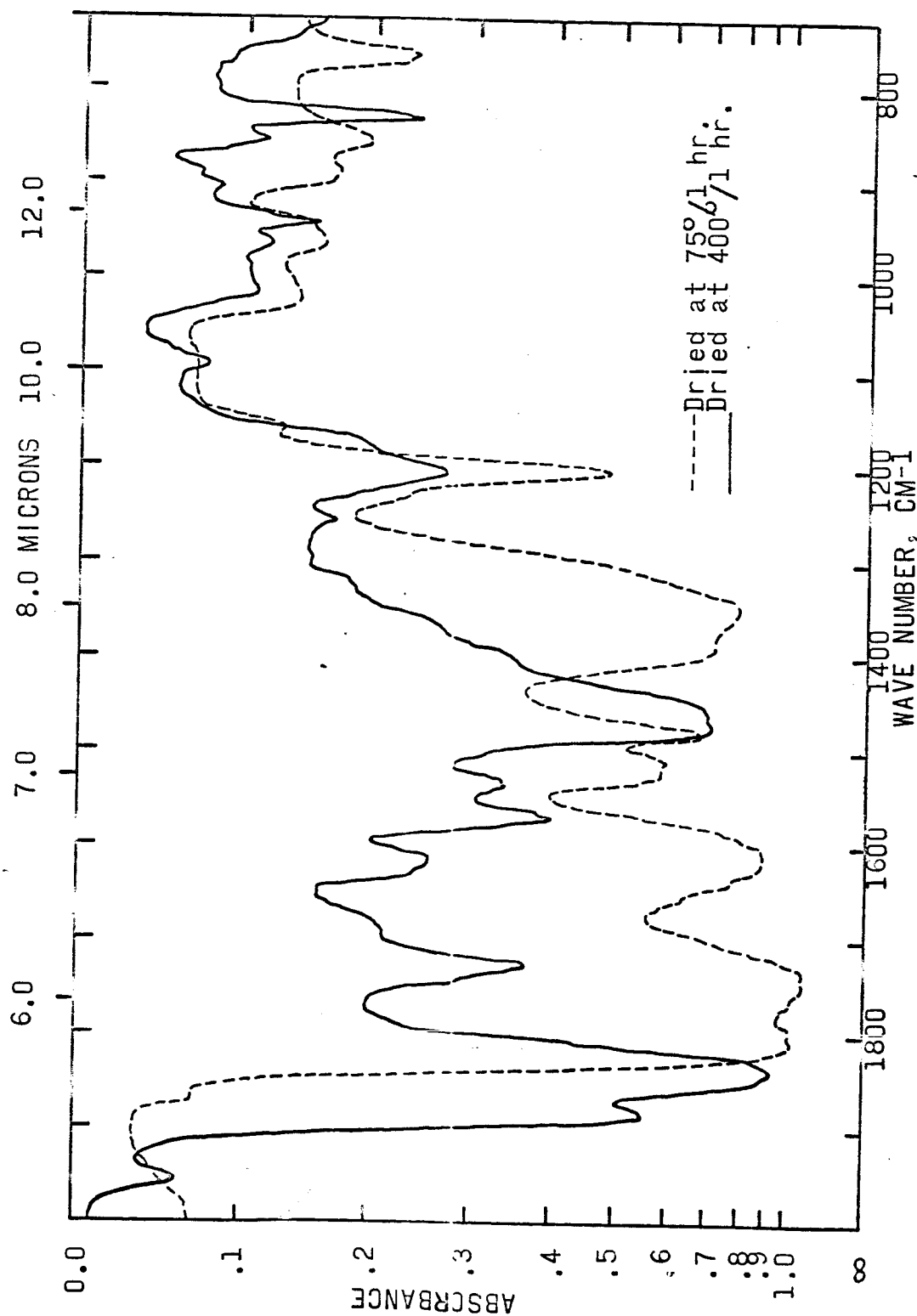
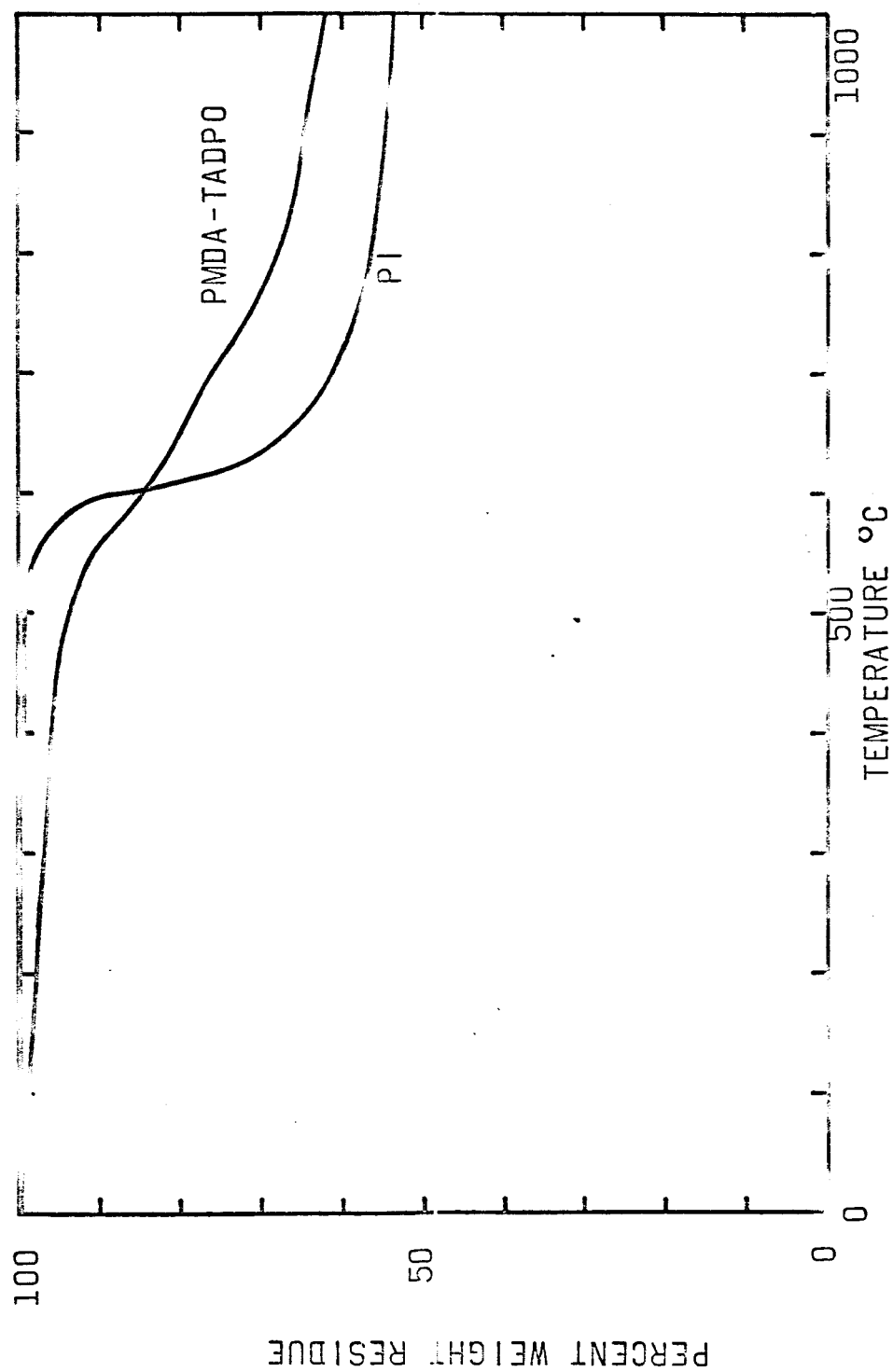


FIGURE 1b. - INFRARED SPECTRA OF PMDA-TAB POLYMER FILMS, 0.15 MIL THICK

FIGURE 2



THERMOGRAVIMETRIC ANALYSIS OF A PYRRONE
AND POLYIMIDE IN VACUUM